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Application of Corona Destruction as a Method to Control Volatile Organic Compounds

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16. ABSTRACT The paper discusses EPA tests of two types of corona reactors. One makes use of a bed of ferroelectric pellets across which an alternating current electric field is impressed. The other develops corona between two electrodes that have been energized by a fast rise time (nanosecond range) electric field. Data from the experiments to date show that the destruction efficiency for toluene at optimum conditions was ≥ 99% in both the packed-bed and the pulsed reactor and that the corona reaction occurs at ambient temperature.

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Electric Corona	Corona Destruction	20C
Organic Compounds	Volatile Organic Compounds (VOCs)	07C
Volatility		

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The Application of Corona Destruction as a Method to Control Volatile Organic Compounds

by

Geddes H. Ramsey, Norman Plaks, Wade H. Ponder, Bobby E. Daniel
Air and Energy Engineering Research Laboratory
Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Larry E. Hamel
Acurex Corporation
P. O. Box 13109
Research Triangle Park, North Carolina 27709

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INTRODUCTION

The EPA interest in corona destruction of molecular species started with modeling of a point-plane reactor for destruction of toxic and other noxious substances[1]. The emerging concern for ozone non-attainment, for which many volatile organic compounds (VOCs) are a precursor, the need to improve technology to control low concentration streams, and the economic advantages of ambient temperature operation provided impetus for the work on high intensity corona reactor devices.

The purpose of this work is to determine if VOCs can be destroyed in these high intensity corona reactors. In setting up the original feasibility-of-concept experiments, an attempt was made to relate the work to the greatest extent possible to current problems threatening the environment. The destruction of both non-halogenated and halogenated compounds has been evaluated. The non-halogenated hydrocarbon was toluene. Toluene was chosen because it is a common solvent of the type implicated in ozone non-attainment. A second consideration was that toluene is a wood smoke surrogate. The halogenated compounds were methylene chloride, which is a common solvent, and CFC-113, a solvent commonly used in the electronics industry, both of which have been implicated in stratospheric ozone layer destruction.

This paper will present a description of the technology, a description of the results, several hypotheses of the reaction mechanisms occurring in the process, and a listing of additional experiments proposed for the future to support these hypotheses.

TECHNOLOGY DESCRIPTION

Two types of corona reactors are being evaluated. The first type makes use of a bed of ferroelectric pellets across which an alternating current (AC) electric field is impressed. The second develops corona between two electrodes that have been energized by a fast rise time (nanosecond range) electric field.

The pelletized bed reactor is shown in Figure 1. The pellets must be made of a material with a high dielectric constant. In this case the material is barium titanate with a dielectric constant of about 6000. Porous stainless steel plates, through which the gas enters and exits the bed, are the

electrodes to which the source of AC voltage is applied. Corona appears between the contact points of the pellets with the application of an external AC electric field that is as low as about 1 kV/cm. Sparking across the bed occurs for fields of 5 to 8 kV/cm, depending upon the size of the pellets. The best operating point for the reactor is just under sparking. The static field from the application of an external direct current (DC) voltage, rather than AC, causes sparking across the bed rather than corona.

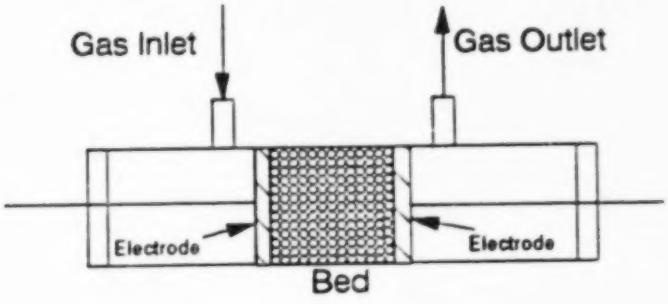

Figure 1: Corona destruction reactor.

In a particle layer across which an electric field has been impressed, the local fields between the particles are greater than the average applied field. Furthermore the local electric fields increase with increasing particle dielectric constant[2]. Very strong fields are developed between the beads or pellets in the direction of the applied field. An analysis based upon application of Paschen's Law, to determine the voltage required for spark breakdown for the pellet geometry, suggests that the electric field in the interstitial spaces between the pellets ranges from 20 to more than 600 kV/cm.

The second reactor, which is of the pulsed corona type, is shown in Figure 2. The gap space between the electrodes, through which a very short (nanosecond pulse) high field strength pulse is impressed, does not contain pellets or any other packing material. The pulse energization system, as shown in Figure 3, consists of a DC power source, a pulse forming network, R_1 and C_1, a rotary spark gap acting as a high voltage switch, and a pulse length forming resistor, R_2. The very rapid discharge of capacitor C_1 provides the very fast rise time pulse. The pulse

repetition rate is set by the rotational speed of the rotary spark gap. Based upon the peak applied pulse voltage and the geometry of the reactor electrodes, electric fields on the order of 20 kV/cm or more can easily be developed[2].

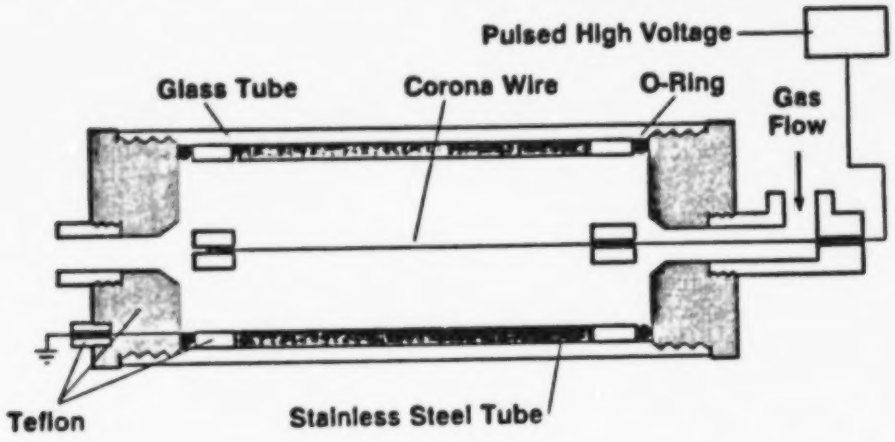

Figure 2. Schematic of pulsed corona reactor.

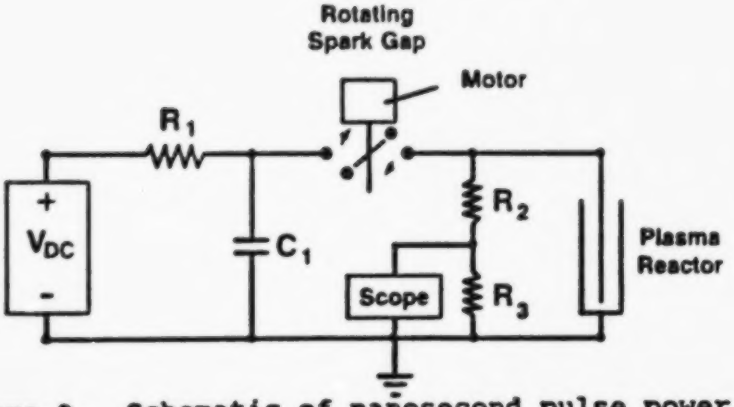

Figure 3. Schematic of nanosecond pulse power supply.

Table I shows the concentrations of the major components in the entering and exiting gas streams for a typical run in the pellet bed reactor.

TABLE I. MAJOR COMPONENT CONCENTRATIONS FOR A TYPICAL RUN IN THE PELLET BED REACTOR

Gas Component	Concentration ppm	
	Inlet	Outlet
Toluene	229	Not detected
Carbon Dioxide	300	313
Carbon Monoxide	Not detected	584

Test conditions: 800 cm^3/min and 14 kV

RESULTS

The first phase of the corona destruction program was to prove that the process could be used to destroy VOCs efficiently. Toluene was chosen as the first compound to be tested. Three pellet sizes (diameters of 1, 3, and 5 mm) were tested. The concentrations of the VOC tested were 60 and 230 ppm. The temperature of the reactor bed and gas stream was maintained at 40°C. The flow rates through the reactor were 200 and 800 cm^3/min. The operating voltages of the reactor were selected based on the sparking voltages for the different size pellets. The maximum voltage was the highest voltage obtainable without sparking, and this voltage was decreased in 2 V increments for the tests. For every set of conditions, five voltages were tested.

When operating at high voltages, a uniform matrix of glow points could be observed over the entire pellet bed with a highly sensitive camera. The camera also allowed the observation of corona onset when it was not evident with the naked eye. The sparking voltage increased with decreasing pellet diameters so the maximum operating voltage was highest with the 1 mm pellets. The maximum destruction efficiency was also obtained with the 1 mm pellets. Figures 4, 5, and 6 show the destruction efficiency for toluene for pellet diameters of 1, 3, and 5 mm, respectively. The toluene molecule is broken down into water, CO_2, and CO. The ratio of CO to CO_2 is on the order of 6:1. Figure 7 shows the amounts of CO produced for the 1 mm diameter pellets. A Hopcolite catalyst was added to the system to oxidize the CO to CO_2 at room temperature. The efficiency of the catalyst was close to 100 percent.

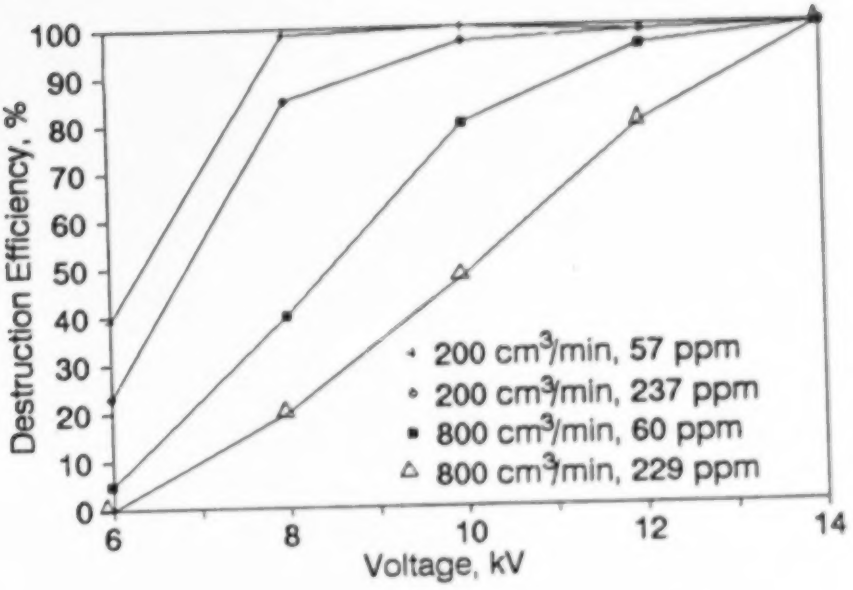

Figure 4. Destruction efficiency for 1 mm pellets.

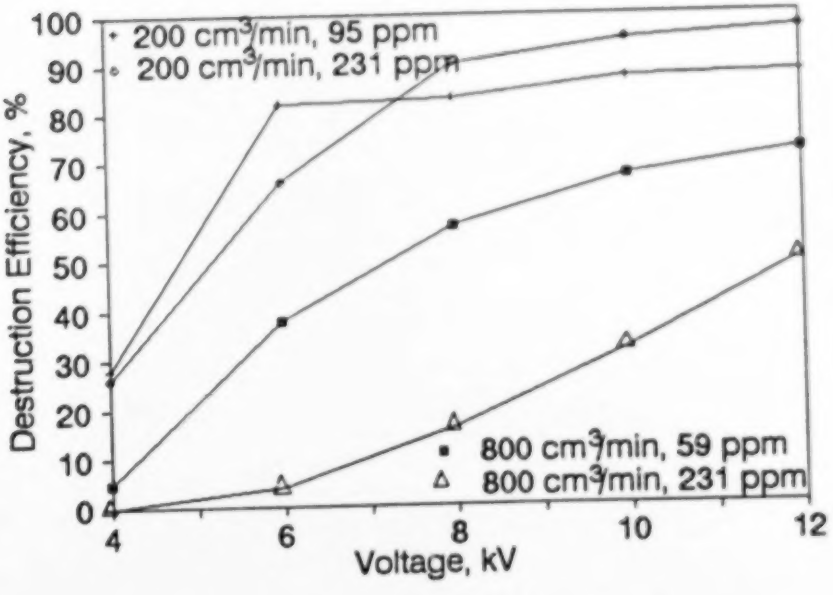

Figure 5. Destruction efficiency for 3 mm pellets.

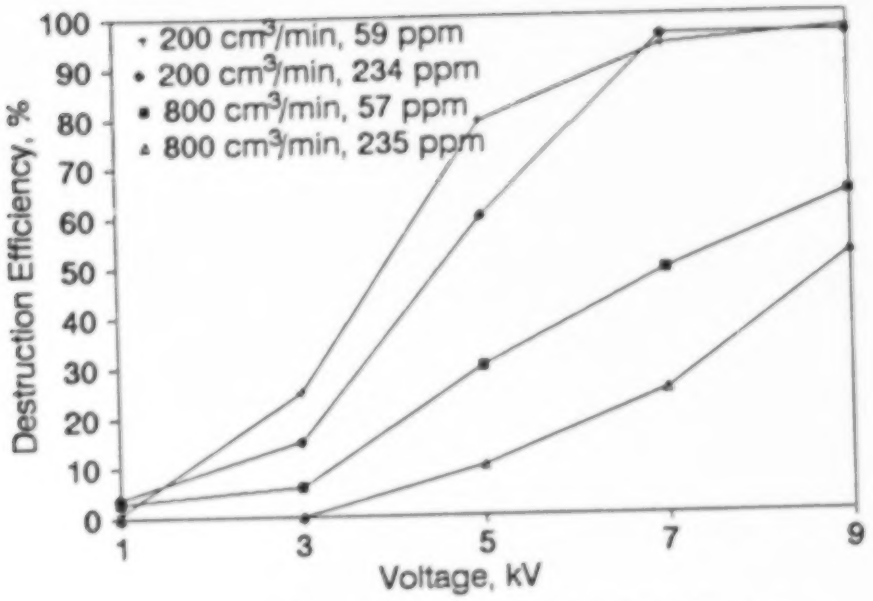

Figure 6. Destruction efficiency for 5 mm pellets.

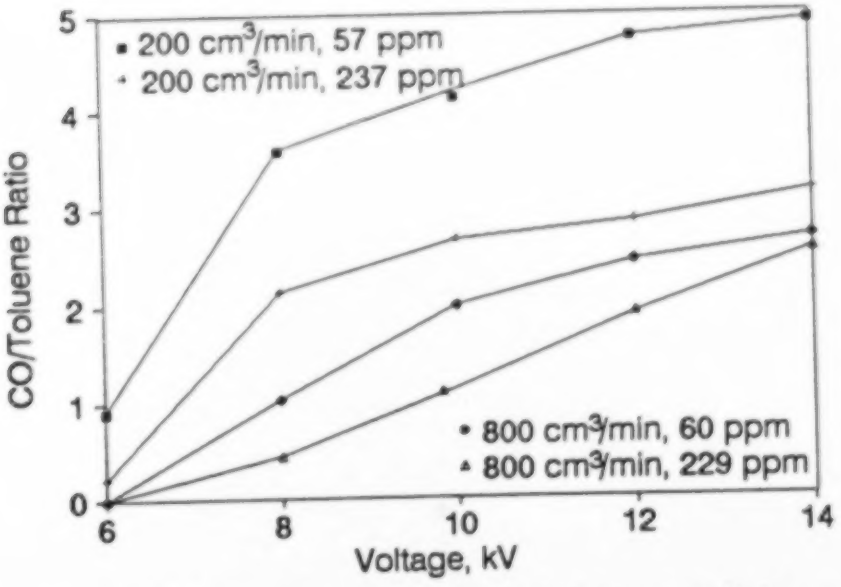

Figure 7. Carbon monoxide/toluene for 1 mm pellets.

The waveforms of the voltage and current were also analyzed for power requirements. Figure 8 shows a typical voltage and current trace. The 60 Hz waveforms broke into smaller pulses during the cycle with durations in the nanosecond range. The phase angle used for the power requirements can be determined from this plot. The power is calculated from:

$$P = VI\cos\theta$$

The power requirements for the most efficient runs were typically in the range of 0.13-0.20 W. The power factor varied with the different pellets and voltages, but typical values were in the 0.14 to 0.22 range.

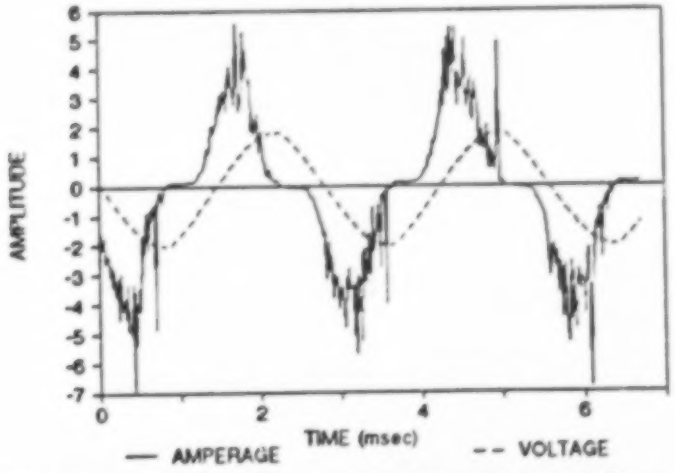

Figure 8. Typical voltage-curent wave form.

From the statistically designed experiment, the following conclusions were evident:

- Of the three pellet sizes (1, 3, and 5 mm) tested, the 1 mm diameter pellets destroyed toluene most efficiently.
- Toluene was apparently destroyed in the reaction. Other than CO, no products of incomplete reaction were identified in the analyses.
- The destruction efficiency for toluene at optimum conditions was greater than 99 percent in both the packed bed and the pulsed reactor.

- The reaction favors the formation of carbon monoxide over carbon dioxide.

THEORY

Electrons undergo both elastic and inelastic collisions during their capricious wanderings. In an elastic collision the electron retains the majority of its kinetic energy. Under the influence of the strong electric field, free electrons are accelerated. They undergo elastic collisions at the end of each free path length. The electrons continue to increase in energy until the energy becomes high enough to allow the electrons to undergo an inelastic collision. During an inelastic collision the electron transfers all or part of its kinetic energy to the particle with which it has collided. In addition, inelastic collisions result in a change to the target particle or molecule such as ionization, disassociation, or excitation[3]. In an inelastic collision significant amounts of energy are transferred from the electron to the target species. Examples of these inelastic collisions are:

- Electron attachment by electronegative gases to form negative ions
- Disassociation of molecular species into smaller fragments including formation of free radicals
- Excitation of molecular and elemental species
- Ionization to form positive ions and additional free electrons (under favorable circumstances a Townsend avalanche develops, generating many additional free electrons)
- Breaking down of molecular species into their elemental and atomic components.

The amount of energy required for the above events varies by type of event and molecular/elemental species. According to the literature, some examples of energy requirements for different types of events are less than 5 eV for electron attachment and 5-25 eV to form positive ions by electron removal[4]. An electron volt (eV) is defined as the energy that an electron acquires (or loses) in passing through a 1 V change. One electron volt is equivalent to 1.6×10^{-19} J or 3.8×10^{-23} kcal. The electron volt is a particularly useful unit of measure for this work because it allows an easily made comparison of electrical energy input to energy requirements for reaction of the target molecules. The probability of one of the above events occurring is expressed by

the collision cross section which is mainly a function of concentration. Whether the event will occur is dependent on the electron's having achieved the energy level needed for the event to occur.

The general velocity of electrons in the direction of the electric field is known as the drift velocity[5]. At atmospheric pressure and ambient temperatures, an electron's energy level can increase by about 1 eV in one mean free path length, if the mean free path length is parallel to an electric field of 20-30 kV/cm. At atmospheric pressure and ambient temperature a mean free path length is about 1×10^{-7} m.

In addition to the above effects of inelastic electron collisions there are also photoelectric effects (ionization, disassociation, excitation, etc.) which are either activated by or result in the emission of a photon. The events that can occur are very much interrelated.

In total the picture that is presented is one of extremely high complexity when the possibility of electron collisions and the effects of photons are considered. The energy distribution in a swarm of energetic electrons ranges from very low to very high, with the majority centered around some median value. Therefore electrons having a wide range of energies will undergo various types of inelastic collisions such as attachment, excitation, and ionization. For a mixture of gases the picture becomes even more complex.

Based on the complexity of the events occurring in the multicomponent gas mixture in the reactor, the dominant mechanism is probably the excitation of the oxygen molecule by the electrons. Since oxygen is the most abundant component of the gas stream that can be excited by the limited amount of energy inputted to the system, the oxygen should provide the required energy to destroy the VOC molecule. The energy inputted is not high enough to affect the nitrogen in the gas. The oxygen, in the form of O, O^-, O_2^-, or excited O_2, initiates the reaction of the hydrocarbon molecule. The potential energies for the ground state and for the first four electronically excited states of O_2 are shown in Table II[6].

TABLE II. THE POTENTIAL ENERGIES FOR THE EXCITED STATES OF OXYGEN

State of oxygen molecule	Energy required eV	Comments
Ground state	0	
1st excitation	0.98	Forbidden transition
2nd excitation	1.63	Allowed; half-life of about 10 seconds collisionally relaxing to 1st excitation state.
3rd excitation	4.25	Theoretically forbidden
4th excitation	6.00	Allowed; creates two oxygen atoms in the ground state via a non-radiative transition.

DISCUSSION

The reaction mechanism and intermediate radicals produced may be comparable to both catalyzed and combustion reactions. The major difference is the low temperature at which it occurs. Catalyzed oxidation reactions require initiation to occur; afterwards they are generally self sustaining. Oxidation by combustion raises the temperature of the bulk gas as well as the molecules to be combusted. Combustion requires a sufficiently high concentration of the fuel to sustain the combustion. Corona destruction, in which the concentration is below the flammability limit, may raise the temperature of individual molecules without affecting the temperature of the bulk gas[4].

When the toluene concentration was about 200 ppm and the energy input was about 10 eV per molecule, the destruction was essentially 100 percent complete. The energy required to initiate the destruction reaction ranged from about 1.4 to slightly over 5 eV which was about 14 to 50 percent of the total supplied as electrical input. The fate of the other 50 to 86 percent of the input energy is unknown. Obviously some portion was used to make ions which because of their low energies do not contribute significantly to the reactions, but due to their drift velocities do expend energy. There is an expenditure of energy as photons as evidenced by the visible corona. Some unknown side reactions very likely occur that do not enter the toluene destruction reaction. Finally some of the energy is being

dissipated as heat both from electron and ion bombardment and from the dissipation factor in the dielectric pellets.

For higher concentrations of toluene(400 ppm), the energy available for each toluene molecule would be about 5 eV; the total power input does not vary with changing concentration. If a significant fraction of the energy inputted goes to support other activities that do not contribute to the destruction of the toluene, then there will not be sufficient energy available to initiate the destruction of all of the toluene.

The data suggest that for a non-halogenated VOC such as toluene the destruction of each molecule must be initiated, after which the molecule will continue to oxidize. For higher concentrations, which are still below the flammable limit, the destruction efficiency will be energy input limited.

For halogenated VOCs the data suggest that, because the reaction is endothermic, the efficiency of the destruction is directly related to the electrical energy that is inputted. It is necessary to strip the halogens from the molecule as part of the destruction. Little is currently known about the intermediate and final by-products.

SUMMATION

- The energy supplied to the corona reactor is not sufficient to break all the bonds in a toluene molecule.
- The corona reactor provides energy to initiate a reaction of the toluene molecule. Once initiated, the reaction proceeds to completion.
- Once initiated the reaction of the toluene molecule proceeds as a low temperature reaction with little or no effect upon other toluene molecules. The reaction is unlike combustion in which the bulk gas temperature rises to a sufficient level to initiate oxidation of other molecules.
- The most probable initiation reaction for destruction of the VOC is attack by an excited oxygen species. Other possible reactions require higher initiation energy.
- The low temperature of the corona destruction process favors the formation of CO over CO_2.
- Halogenated compounds require energy to strip the halogens from the molecule for destruction of the molecule. The fate of the by-products of the destruction requires additional study.

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